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14. ABSTRACT
The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

15. SUBJECT TERMS
corrosion protection, self-healing, coatings, polymers

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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #4

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1 Summary

Paint characterization has resumed, with the OTS-rich microcapsules performing on par with similar samples tested last year. In the ongoing quest to eliminate the need for freeze-drying, we observed that OTS-rich microcapsules filter, dry, and redisperse better than GPS-rich microcapsules. We are exploring the use of aminated surfactants to improve the dispersability of the dry microcapsules without degrading the adhesion of the paints.

2 Project Goals and Objectives

The kickoff meeting was held on March 12th with representatives from ONR, PPG, and APL. We have decided to push back our schedule to account for the interruption in funding. According to the new schedule, the Polyfibroblast formulation will be finalized in August and the field test will occur in early 2013.

3 Key Accomplishments

3.1 OTS-Rich Microcapsules

Two of the best performing formulations from FY11 were the 25% OTS and 35% OTS samples. We hypothesized that the good performance was due to the formation of hydrophobic self-assembled monolayers by the OTS molecule. This hypothesis was supported by the fact that OTS-rich microcapsules tend to perform best when only 5 vol% of the filler (or about 2.5% of the total volume of the paint) consists of microcapsules.

This month we repeated the test with the 8-month-old 35% OTS sample to check for reproducibility. We also tried 45% OTS microcapsules. Although harder to synthesize, microcapsules with higher OTS concentration are expected to perform better since more OTS is available to passivate the exposed steel. Moisture resistance results comparing last year's data to this year's data are given in Figure 1. The performance is pretty consistent. When only 5% microcapsules are used, we see no rust except in the wide 0.125 inch scratch. The performance generally gets worse with increased microcapsule loading, except in one case where the 35% OTS sample received a perfect score (no rust) with a 50% microcapsule loading.

Higher microcapsule loading appears to break up the Zn packing such that only the Zn particles close to the scratch contribute to galvanic protection. These are quickly consumed, allowing rust to form in only 24 hours. When the filler is 95% zinc, the Zn particles are able to make good electrical contact with each other and act like a single, sacrificial anode. The small amount of OTS appears to passivate enough of the exposed steel to improve performance relative to 100% zinc, but yet the presence of microcapsules does not appear to reduce the galvanic protection even when they completely fail to heal the scratch. From a practical standpoint, this is the best possible outcome. **5 vol% microcapsule loading corresponds to about 1.7 ounces of microcapsules per gallon of paint!** Even if the chemicals and processing are relatively expensive, such small amounts are less likely to affect the total cost of the paint.

The bottom line from these experiments was that last year's excellent salt fog results for the 25% OTS and 35% OTS were probably not an aberration. We can say that shelf life is at least 8 months. We can also say with more confidence that OTS-rich microcapsules used in conjunction with 95% zinc powder as the filler will provide good protection against rust when scratched.

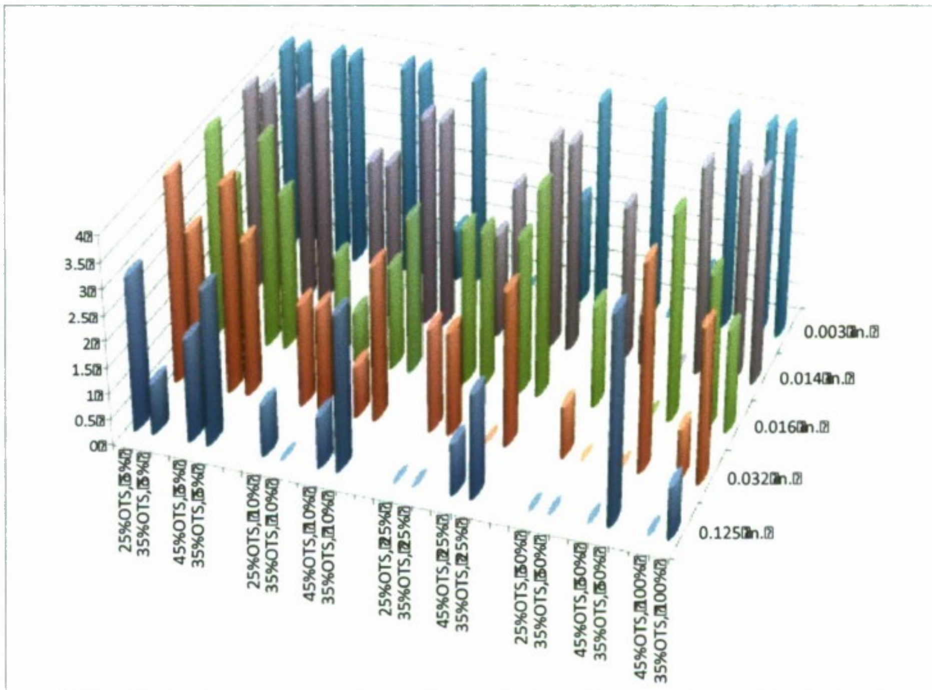

Figure 1: *Rust scores for OTS-rich microcapsules. The 25% OTS and 35% OTS samples are from last year, and the 45% OTS and 35% OTS samples are from this year.*

	Rust Score				
Sample Name	**0.125 in.**	**0.032 in.**	**0.016 in.**	**0.014 in.**	**0.003 in.**
25%OTS, 5% ucaps	3	**4**	**4**	**4**	**4**
35%OTS, 5% ucaps	1	**3**	**3**	**4**	**4**
45%OTS, 5% ucaps	2	**4**	**4**	**4**	**4**
35%OTS, 5% ucaps	3	**3**	**3**	**4**	**4**
25%OTS, 10% ucaps	1	2	2	3	4
35%OTS, 10% ucaps	0	2	1	3	4
45%OTS, 10% ucaps	1	1	2	4	1
35%OTS, 10% ucaps	3	3	3	4	4
25%OTS, 25% ucaps	0	2	3	2	0
35%OTS, 25% ucaps	0	2	3	3	2
45%OTS, 25% ucaps	1	0	3	4	2
35%OTS, 25% ucaps	2	3	4	4	4
25%OTS, 50% ucaps	0	1	2	3	4
35%OTS, 50% ucaps	**0**	**0**	**0**	**1**	**0**
45%OTS, 50% ucaps	0	0	0	0	1
35%OTS, 50% ucaps	**4**	**4**	**4**	**4**	**4**
45%OTS, 100% ucaps	0	1	3	4	4
35%OTS, 100% ucaps	1	3	2	4	4

Table I: Rust score data corresponding to Figure 1. Note the good performance for the samples with only 5% microcapsules, and the discrepancy between the two 35% OTS samples.

3.2 Filter, Air-Dry, and Redisperse

Unfortunately, filtering and air-drying samples still does not produce the same quality results as freeze-drying. OTS-rich microcapsules were shown to redisperse fairly well after air-drying, so long as silica nanopowder was added as an anti-caking agent. GPS-loaded microcapsules appear to cake irreversibly even with the added nanopowder. This discrepancy may be due to the fact that OTS does not polymerize as readily as IPDI. The OTS-rich microcapsules may break during filtration, but the OTS does not glue the microcapsules together. The GPS-loaded microcapsules, on the other hand, are primarily IPDI. If any of these microcapsules break during filtration, the IPDI will polymerize and make it impossible to redisperse them. We are therefore revisiting the idea of using surfactants to improve the dispersability of the dry microcapsules that are allowed to air-dry.

Previously, the use of C12E4 surfactant during filtration resulted in some of the best free-flowing powders made to date. Unfortunately, the C12E4 residue caused a noticeable loss of adhesion in the primer. To combat this problem, we propose the use of surfactants with primary amines as the hydrophilic head group. The primary amine will be positively charged in water at neutral pH, and it will react instantly with free isocyanate to form a urea. The surfactant will not, however, polymerize with isocyanates because it has only one amine group. It will instead act like an end cap, preventing polymerization, and otherwise scavenging free isocyanates present on the microcapsules.

This scavenging action can be especially beneficial if any microcapsules rupture during filtration. It is believed that a small fraction of microcapsules do rupture during this process. This free isocyanate monomer will then polymerize while the microcapsules dry in air. We believe that such polymerization is the primary reason that the filtered microcapsules do not redisperse. If any amine-functional surfactant still remains after drying, it will be consumed by the primer when the microcapsules are mixed into the polyurethane resin. We therefore would not expect the amine-functionalized surfactants to have any negative impact on adhesion.

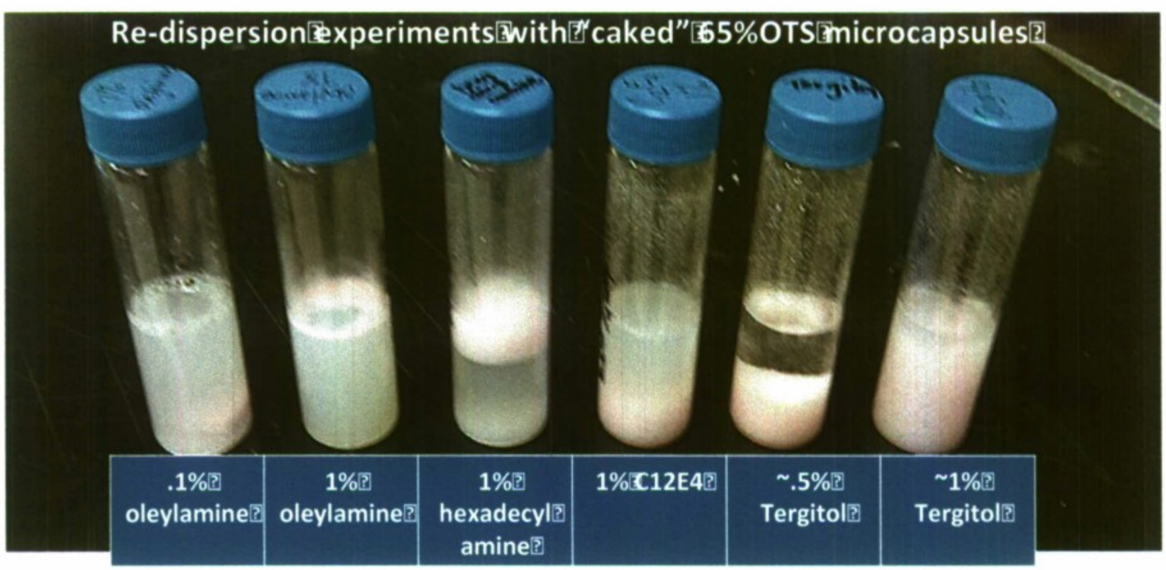

Figure 2: *65% OTS microcapsules redispersed using a series of surfactants after air-drying.*

Figure 2 compares the ability of several different surfactants to redisperse microcapsules in water after air-drying. Although not a direct measure of anti-caking ability, this quick test provides insight into the ability of a surfactant to prevent agglomeration or promote dispersion. We found that the long chain amine surfactants did not disperse the caked microcapsules as well as the nonionic surfactants. Oleylamine has 18 carbons, and hexadecylamine has 16. These surfactants are so hydrophobic that they only dissolve at low pH. It remains unclear whether the pH change causes microcapsule rupture, but so far these surfactants have displayed poor anti-caking ability. Possibly, the low water solubility may also mean that they do not decrease surface tension enough to prevent agglomeration during drying. We are therefore currently exploring short-chain amines with 6 carbons or less that are completely miscible in water at neutral pH.

3.3 Kickoff Meeting

The FY13 kickoff meeting was held at JHU/APL on March 13th. In attendance were the APL team, Cody Reese from ONR, and Stu Hellring, Scott Benton, and Ed Rakiewicz from PPG. After reviewing the FY13 research plan, we agreed to move our schedule back by about 6 months due to the recent interruption in funding. Rather than finalize the formulation in April, the milestone has been shifted to August. The field test in Camp Lejeune will therefore occur sometime in December or January. After this meeting, we followed up with Andrew Sheetz from the USMC Corrosion Control Team to confirm that the change in schedule would be accommodated. Andrew also confirmed that the field test would consist of normal wear and tear on a MTVR and that the performance will primarily be evaluated by periodic visual inspection of the vehicle.

At the meeting we also discussed a possible transition path through the JLTV program. APL has been in talks with the USMC program manager for that program, and Polyfibroblast received positive feedback after the briefing earlier this month.

3.4 Publication in PCI Magazine

Polyfibroblast is featured in this month's issue of PCI magazine (Paint & Coatings Industry). The article "Self-Healing Coatings with Galvanic Protection" describes the results from the first year of this program.

http://www.pcimag.com/articles/96150-self-healing-coatings-with-galvanic-protection-

We plan to submit a more detailed article on this work to a peer-reviewed journal in the near future.

4 Next Steps

4.1 Performance Optimization

For the next few months APL will continue to explore different combinations of silane type, silane concentration, and zinc powder concentration until we are confident that we have

optimized the corrosion protection. Processing improvements, such as air-drying, will continue to be pursued, but those efforts will not take priority over performance optimizations.

4.2 Continuous Rotor-Stator

PPG will be coming online this month. They will be transitioning from a batch rotor stator mixer to a continuous rotor stator mixer. First they will work with the original Polyfibroblast formulation to isolate the impact of the new mixer before moving on to modified formulations.